Chemical Physics 538 (2020) 110862

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Investigation of pressure effects on melting temperature and shear modulus of B1-LiF

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ARTICLE INFO

Keywords:
Melting curve
Shear modulus
High pressure
Debye model
Lindemann criterion

ABSTRACT

The pressure effects on melting temperature and shear modulus of the B1 phase of LiF are investigated based on a semi-empirical approach. We derived analytical expressions of these quantities as functions of pressure. Numerical calculations are performed for LiF up to pressure of 100 GPa. Our work reveals that the melting curve derived from the Simon-Glatzel equation shows a high gradient at pressure below 30 GPa and rather quickly flattens with the increasing of pressure in accord with experiments, much more precise than the calculations based on the Lindemann melting criterion and the power-law of Grüneisen parameter. Meanwhile, the pressure-dependent shear modulus derived from Burakovsky's model and the power-law of Grüneisen parameter shows a good agreement with ab initio calculations. Our results provide a further supplement to the database of high-pressure melting temperature and shear modulus of LiF. The present work could be used to verify as well as analyze the future high-pressure experiments.

1. Introduction

Lithium fluoride (LiF) is an ionic crystal and an insulator with B1 structure (NaCl type) at ambient pressure and temperature. Previous works showed that LiF remains stable in the B1 phase up to pressure greater than 100 GPa [1,2]. This crystal is one of the largest optical gap solids (above 11 eV) and it is an optically transparent insulator which is predicted to remain transparent up to pressure of 200 GPa [3]. This property of LiF allows it to be widely used as a window material through which to carry out wave profile measurements for dynamic compression experiments. Furthermore, LiF can be used as a pressure-transmitting medium and a pressure calibrant in static compression measurements on a diamond anvil cell (DAC) [4]. Due to these above applications, investigation of physical properties of LiF at high pressure becomes a subject attracting the attention from a broad experimental research community [5,6].

With remarkable developments of experimental techniques, researchers could perform various methods to measure the pressure-volume data (e.g., equation-of-state) [7], refractive index [8], melting temperature [2],…of LiF up to hundreds of GPa in order to optimize its application as an interferometer window. On the theoretical side, numerous approaches were employed to predict high-pressure thermodynamic properties, mechanical properties, optical properties and phase transition of LiF such as first-principles calculations [9–11], ab initio many-body Green's function calculations [6], molecular dynamics (MD) simulations [12,13]. However, to the best of our knowledge, the prediction of high-pressure melting point of LiF is still under debate and disagreement among different methods such as DAC experiment [2], MD simulations [12,13], and ab initio calculations [10]. Moreover, there is seemly no experimental measurement for the shear modulus of LiF at high pressure.

In present study, with the aim of contributing to the database of high-pressure physical properties of LiF crystal, we present a semi-empirical approach to investigate the pressure effects on its shear modulus and melting temperature. Numerical calculations are performed up to pressure of 100 GPa in which the LiF crystal is in the B1 phase. Our theoretical results are compared with those of previous published data when possible to verify theory.

We organize this paper as follows, in Section 2, we present a theoretical approach to study thermo-mechanical properties of LiF which are solved numerically. In Section 3, we discuss numerical results in detail followed by Section 4 in which we make the conclusions of the paper.

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https://doi.org/10.1016/j.chemphys.2020.110862
Received 17 February 2020; Received in revised form 15 May 2020; Accepted 27 May 2020

2. Theory

In this work, the pressure effects on the shear modulus and the melting temperature of LiF are studied by considering the relations between these thermodynamic quantities and Grüneisen parameter. Regarding to the melting problem, the most widespread theory has been applied for the investigation of melting is the Lindemann melting criterion [14–17]. This criterion was stated that “A material starts to melt when the ratio between atomic mean-square vibration and square of nearest-neighbor distance reaches a threshold value” [18]. This threshold value is characteristic for each material. Previous works showed that Lindemann melting criterion can be re-written as the following melting formula [19,20]

$$T_m = \text{const} \times V^{\frac{2}{3}}.\ \theta_D^2, \tag{1}$$

where T_m, V and θ_D are the melting temperature of material, crystal volume and Debye temperature, respectively.

From Eq. (1), we can easily derive it into the equation

$$\frac{\partial \ln(T_m)}{\partial V} = \frac{2}{V}\left(\frac{1}{3} - \gamma_G\right), \tag{2}$$

where $\gamma_G = -\partial \ln\theta_D/\partial \ln V$ is the Grüneisen parameter in Debye model. The Grüneisen parameter was proposed by Grüneisen [21] to describe the volume dependence of phonon frequencies ω_i as $\gamma_G = -\sum_i \frac{\partial \ln\omega_i}{\partial \ln V}$. Previous works showed that the Grüneisen parameter can be seen as constant at low pressure, and it reduces gradually when pressure increases [22–24]. Some experimental results proposed the law $\gamma_G/V = \text{const.}$ [25] More general form of the Grüneisen parameter suggested by Graf et al. [26] is

$$\gamma_G = \gamma_0\left(\frac{V}{V_0}\right)^q = \gamma_0\eta^q, \quad q > 0, \tag{3}$$

where γ_0 and V_0 are the Grüneisen parameter and crystal volume at zero pressure, respectively; and $\eta = V/V_0$ is a volume compression [26,19]. This power-law form described well the pressure-dependent Grüneisen parameters of copper and gold metals, and was successfully applied to investigate the pressure dependence of mean-square displacements of these noble metals [26]. It should be noted that, the simple law $\gamma_G/V = \text{const}$ is a particular case of Eq. (3) when $q = 1$ is applied.

Substituting Eq. (3) into Eq. (2) and taking integral, we derived the expression of melting T_m as a function of volume compression η as

$$T_m = T_0\eta^{2/3}\exp\left[\frac{2\gamma_0}{q}(1 - \eta^q)\right], \tag{4}$$

where T_0 is the melting temperature of material at ambient conditions.

Now we consider the pressure dependence of the shear modulus based on its relation with the Grüneisen parameter. There are many analytic models describing this relation such as Guinan and Steinberg model [27], and Preston and Wallace model [28]. In current paper we use a model proposed by Burakovsky et al. [29,30] as

$$\gamma_G = -\frac{1}{2}\frac{\partial \ln G}{\partial \ln V} - \frac{1}{6}. \tag{5}$$

Here it should be noted that the Lindemann melting criterion requires volume dependence of $\theta_D(-2, V)$ which is proportional to the second frequency moment of atomic vibrations, while Eq. (5) of shear modulus G has a relation with $\theta_D(-3, V)$. For simplicity, in this work, we make an assumption that $\theta_D(-2, V) \approx \theta_D(-3, V) \approx \theta_D$ or $\gamma_G(-2, V) \approx \gamma_G(-3, V) \approx \gamma_G$. Indeed, the assumption was applied by Foata-Prestavoine et al. to investigate the elastic constants, phonon dispersion curves, and melting temperatures of bcc Ta up to 1000 GPa [31]. The authors pointed out that in the relatively high compression range, no highly significant differences (about 10%) are expected when using $\theta_D(-2, V)$ or $\theta_D(-3, V)$ to estimate T_m with the Lindemann melting criterion. It was seen as a fundamental uncertainty in their ab initio calculations.

By substituting the Grüneisen parameter expression Eq.(3) into Eq. (5), and taking integral we derived the following expression of the shear modulus as

$$G = G_0\eta^{-1/3}\exp\left[\frac{2\gamma_0}{q}(1 - \eta^q)\right], \tag{6}$$

where G_0 is the shear modulus at ambient pressure.

Taking into account Eqs. (4) and (6), the volume dependence of the shear modulus and melting temperature of material can be calculated numerically. In order to consider the pressure effects on these physical quantities, we need to know an equation-of-state (EOS) which accurately describes the relation of pressure, volume and temperature of system. Many EOSs have been proposed to study thermodynamic properties as well as phase transitions of solids at high pressure such as Birch-Murnaghan EOS [32], Holzapfel EOS [33]…In the work of Cohen et al. [34], the Vinet equation is found to be the most accurate EOS at high compressions, and it will be used in this paper. The well-established Vinet EOS has the form as [35]

$$P = 3B_0\eta^{-2/3}(1 - \eta^{1/3}) \times \exp\left[\frac{3}{2}(B_1 - 1)(1 - \eta^{1/3})\right], \tag{7}$$

where B_0 and B_1 are correspondingly the isothermal bulk modulus and its first-pressure derivative.

3. Results and discussion

In the following, the expressions established in the previous section are applied to calculate numerically shear modulus and melting temperature of LiF crystal. By using the experimental measurements of bulk sound velocities and the Hugoniot data to determine Grüneisen parameter of LiF, Liu et al. [36] showed that all calculated data points of Grüneisen parameter can be fitted with a power-law function as $\gamma_G = \gamma_0\eta^{0.842}$. It means that in Eq. (3), parameter q is equal to 0.842 for LiF. The melting temperature of LiF at ambient pressure is $T_0 = 1113$ K [37]. From synchrotron radiation X-ray powder diffraction and a DAC, Liu et al. [4] determined EOS and thermal expansivity of LiF up to pressure of 37 GPa and derived experimental data of isothermal bulk modulus as $B_0 = 73.04$ GPa and $B_1 = 3.90$.

Using Eq. (4), numerical calculations of melting temperature T_m (dashed line) are performed for LiF up to pressure of 100 GPa and then plotted in Fig. 1. By performing MD simulations of the melting and/or freezing of LiF, Belonoshko et al. showed that the B1–B2 transition in

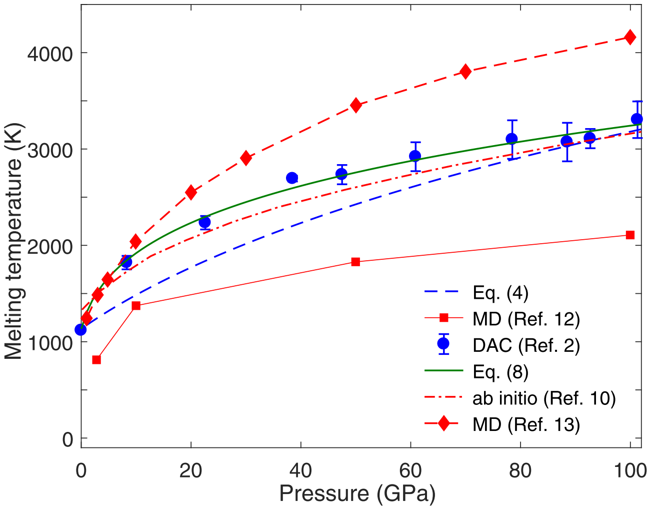

Fig. 1. Melting curves T_m of LiF in B1 structure up to pressure 100 GPa. Our melting lines are compared with DAC experimental data [2], ab initio calculations [10], and MD simulations [12,13].

LiF at around 100 GPa removes the discrepancy between the DAC and shock-wave melting temperatures [12]. The DAC experimental data (closed circles with error bars) measured by Boehler et al. [2], ab initio calculations (dashed-dotted line) [10] and MD simulations (closed squares and closed diamonds) [12,13] are also shown for comparison. As it can be seen from the Fig. 1, while ab initio calculations go along with experimental data, the results calculated from Lindemann melting criterion are just in good agreement with measurements beyond pressure of 80 GPa. At pressure below 80 GPa, our theoretical calculations underestimate the data of DAC experiment, especially at pressure of about 20 GPa. At this pressure, the melting slope dT_m/dP of Lindemann melting line is significantly different from the DAC melting data of LiF. Especially, two MD simulations [12,13] show large deviations from our calculations as well as DAC measurements of Boehler et al. [2]. At pressure 100 GPa, the differences between MD simulations and DAC results are about 1000 K. These discrepancies at high pressure were explained that the pair-wise Tosi-Fumi [12] and Buckingham [13] potentials are inappropriate in studying LiF material. Nevertheless, all of the calculated and DAC experimental melting curves of LiF exhibit common features of the pressure-dependent melting line. They increase rapidly at low pressure and flatten considerably at high pressure.

One of the most well-known empirical equations which can represent experimental data for “normal” melting curve is two-parameter Simon-Glatzel equation [38]. It is a rising melting function and has the form as

$$T_m = T_0\left(1 + \frac{P}{a}\right)^b, \tag{8}$$

where a and b are parameters characterizing for studied material.

By fitting DAC melting measurements of LiF [2] to Simon-Glatzel empirical function in the least-square approximation, we obtained two parameters $a = 1.2306$ and $b = 0.2384$. As it can be seen in Fig. 2, the two-parameter Simon-Glatzel equation can well predict the melting point of LiF in all studied pressure range, much more exact than the calculations based on the Lindemann melting criterion. The Simon-Glatzel melting curve (solid line) shows a high gradient at pressure below 30 GPa and rather quickly flattens with the increasing of pressure in accord with DAC experimental measurements.

The difference between high-pressure Lindemann melting curve and experimental data could originate from some reasons: (i) the limitation of Lindemann criterion approach on studying the melting phenomenon of materials at high pressure: Previous studies showed that this criterion works for many materials but not for all of them [39,17]; (ii) the power-law of Eq. (3) may not describe exactly the pressure dependence of Grüneisen parameter of LiF; (iii) the harmonic approximation in the temperature-dependent Debye model has neglected the anharmonicity. This would underestimate the melting temperature of LiF at high-pressure and high-temperature. The controversy requires further calculations with more accurate quantum mechanics techniques.

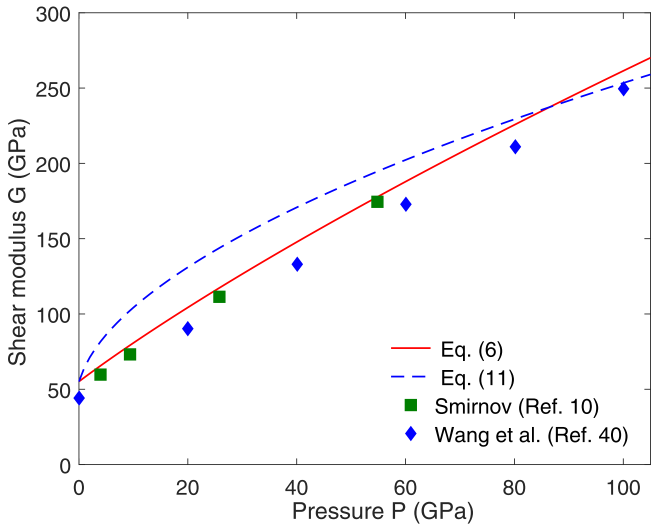

Fig. 2. Shear modulus G of LiF in B1 structure up to pressure of 100 GPa. The results derived from ab initio calculations of elastic constants [10,40] have also been shown for comparison.

It is worth to mention that Eq. (1) of Lindemann melting criterion can also be developed to the following melting equation [23]

$$\frac{\partial \ln(T_m)}{\partial P} = \frac{2}{B_T}\left(\gamma_G - \frac{1}{3}\right), \tag{9}$$

where $B_T = -V(\partial P/\partial V)_T$ is the isothermal bulk modulus.

By substituing Eq. (8) into Eq. (9), we derived an expression of the Grüneisen parameter as a function of pressure P as

$$\gamma_G = \frac{1}{3} + \frac{b}{2}\frac{(B_0 + B_1 P)}{a + P}, \tag{10}$$

where the isothermal bulk modulus $B_T = B_0 + B_1 P$ with B_0 and B_1 are, respectively, the isothermal bulk modulus at ambient pressure and the first pressure-derivative of isothermal bulk modulus.

Combining Eq. (10) with Eq. (5) proposed by Burakovsky et al. [29], we obtained the pressure-dependent shear modulus as

$$G = G_0\left(1 + \frac{B_1}{B_0}P\right)^{1/B_1}\left(1 + \frac{P}{a}\right)^b. \tag{11}$$

By substituting the fitted parameters $a = 1.2306$ and $b = 0.2384$ into Eq. (11) we can easily determine the pressure-dependent shear modulus of LiF. In Fig. 2, we present the shear modulus lines of LiF calculated from Eq.(6) (solid line) and Eq. (11) (dashed line) as functions of pressure up to 100 GPa. The shear modulus results derived from ab initio calculations of elastic constants [10,40] have also been shown for comparison. From this figure we can see that the shear modulus of LiF rapidly increases with the increasing of pressure. Although the calculated shear modulus curve from Eq. (11) has a high gradient at low pressure and rather quickly flattens with increasing pressure, the shear moduli calculated from Eq.(6) are in accordance with those derived from elastic constants in ab initio calculations of Smirnov [10]. The shear moduli derived from Wang et al.’ work show the same behavior but to a somewhat lesser extent. Furthermore, while the shear modulus calculated from Eq. (6) can be well fitted by a quadratic polynomial as $G = 57.68 + 2.33P - 2.81.10^{-3}P^2$ (GPa), the second curve calculated from Eq. (11) is badly fitted by polynomial function with order smaller than 5. The results of shear modulus are significant to geophysical implications. It can be used to calculate as well as analyze the shear wave polarized perpendicular and parallel to the basal plane [41,42]. The present results can be used as reference data for future high-pressure experiments and theoretical works. The discrepancy between two theoretical curves also requires further investigations of the shear modulus of LiF.

4. Conclusions

In this work, the pressure effects on melting curve and shear modulus of the B1 phase of LiF have been studied based on the semi-empirical approach. Our calculations up to pressure of 100 GPa reveals that the melting curve derived from the Simon-Glatzel equation shows a high gradient at pressure below 30 GPa and rather quickly flattens with the increasing of pressure in accord with experiments, much more precise than the calculations based on the Lindemann melting criterion and the power-law of Grüneisen parameter. The latter approach gives the melting line with slope significantly deviating from the experimental data. The combination of Burakovsky’s model and the power-law of Grüneisen parameter gives the pressure-dependent shear modulus which agrees well with ab initio calculations. The present work supplements to the database of high-pressure melting temperature and shear modulus of LiF. The discrepancy between two pressure-dependent shear modulus curves requires further investigations for LiF.

CRediT authorship contribution statement

Nguyen Van Nghia: Data curation, Formal analysis, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Ho Khac Hieu:** Conceptualization, Resources, Validation, Writing - original draft, Writing - review & editing. **Nguyen Ba Duc:** Resources, Project administration, Supervision, Investigation, Writing - original draft, Writing - review & editing. **Trinh Phi Hiep:** Validation, Visualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge two anonymous reviewers for their useful comments and suggestions.

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